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SCANNING ELECTRON MICROSCOPY TO ESTABLISH THE MARBLE WEATHERING MECHANISM IN THE ALHAMBRA OF GRANADA (SPAIN)

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Abstract

The weathering processes of the white marble from Macael quarries (Almería, Spain) used in the Alhambra of Granada have been studied with the aim of establishing the weathering factors and mechanism. Unaltered quarry samples have been submitted to diverse accelerated weathering experiments and their morphology compared to the altered materials from the monument. The weathering process stages have been established and the degree of weathering in some monumental dependencies evaluated.

KEY WORDS: white marble, weathering mechanism, thermohygrometric variations, accelerated tests, Alhambra of Granada, Macael.

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Introduction

White marble from Macael quarries (Almería, Spain) has been widely employed from time immemorial in monumental buildings in the South of Spain due to its artistic and technical qualities and abundance.

From the point of view of its conservation in certain monuments, it is important to know the factors which condition the weathering of the stone and the weathering mechanisms. It is possible to know the weathering factors and mechanisms by accelerated weathering experiments on unaltered material and the later comparison with the altered monument material; however, the accelerated experiments do not produce visible manifestations of weathering in a reasonable period of time, particularly for compact materials like marble. Therefore, it is necessary to resort to the microscopical methods; the use of scanning electron microscopy because it allows observations of the microscopical weathering and their comparison with the monument materials of the tested samples in a reasonable period of time.

Environmental conditions

The city of Granada, 664 m above sea level, is included in the continental region, continental extreme subregion [9], which is characterized by cold winters and very warm summers; the high number of days/year with temperatures lower than 0°C and the great thermic oscillations are important. The relative humidity values oscillate between 30% in July and 90% in January; on the same day, oscillations of 40% in the relative humidity can be registered [5]. In a study carried out during 1988 and 1989 on the Alhambra, thermic oscillations of 30°C in a day have been registered. The environmental conditions in the surroundings of the monument rule out the action of gaseous and particulate atmospheric pollutants on the stony materials which has been verified by X-ray and energy dispersive spectrometry (EDS) studies on monument samples. We consider sulphur and nitrogen oxides as gaseous pollutants with direct influence on stone weathering; they provoke the chemical attack of the $CaCO_3$ with formation of new chemical substances. However, some authors [11] think that it is necessary to consider the direct action of the atmospheric CO_2 which can control the dissolution and precipitation of calcite in aqueous media. Some investigations [7, 8] have demonstrated that a pH lower than 4 is necessary for the effective dissolution of the calcite crystals in aqueous media; only the dissolved CO_2 cannot provoke those pH decreases and for this reason, if sufficient quantities of other acid pollutants are not present, the CO_2 action must not be considered as an important weathering factor.

Visual indicators of weathering

The most characteristic macroscopical morphology of weathering of the white marble from the Alhambra of Granada consists of a very important intercrystal decohesion, which in many cases includes grain disgregation. Those materials located in areas of great public influx show visual indicators derived from the anthropogenic mechanical actions: scrapes, excoriations, strictions, etc. The fact that Granada is located within a high seismicity zone explains the frequent cracks and fissures. The high thermic oscillations and the anisotropic crystallization of the marble have given rise to some situations of plastic deformation.

Materials and Methods

Samples

For this study, some samples from the monument were obtained from some ancient restoration remains; and others were obtained in the "Patio de los Leones" during a previous investigation. A complete study on the whole monument could not be carried out because only samples from some parts of the Alhambra were available; however, we consider that the results presented here are applicable to the general situation of such materials. For the accelerated weathering experiments 5 cm edged cubic samples from the quarries were used.

Apparatus

The study was carried out in a ISI-SS40 Scanning Electron Microscope (SEM) fitted with a Kevex energy dispersive X-ray spectrometer on gold-coated samples. For the artificial accelerated weathering experiments, a climatic chamber CCI FCH-1216 was employed. Mercury intrusion porosimetry measurements were performed with a Carlo Erba 2000 porosimeter. The pore structure was assumed to be made of cylindrical open pores. X-ray powder diffraction (XRD) studies were carried out with a Philips PW-1710 diffractometer using CuK_α radiation and Ni filter.

Accelerated weathering experiments

The basic cycle for the accelerated weathering tests were the thermohygrometric variations from -15 $\pm$ 0.5°C to +80 $\pm$ 5°C and 95% relative humidity (RH); 10 hours of exposure under both conditions and an intermediate stage of 14 hours at laboratory temperature and RH were employed. 80 cycles were carried out. Some samples were submitted to variations from -15°C (for 10 hours) to laboratory conditions (for 38 hours) and others from laboratory conditions (for 38 hours) to 80°C/95% RH (for 10 hours). These subcycles were carried out to identify the laboratory conditions which can closely resemble the influence of weathering in the global cycle. Simultaneously, the influence of freeze/thaw cycles was also tested.

The results of other accelerated weathering experiments that we previously carried out [1, 4], e.g., salt crystallization tests (diverse salts and experimental conditions), high temperatures (100 to 400°C) and chemical attack (H_2SO_4, NH_4HSO_4 and SO_2), are not considered in this work because the weathering micromorphologies obtained do not correspond with the observed ones in the altered materials from the Alhambra.

Results and Discussion

Altered Alhambra Samples

A morphology of characteristic weathering has been established by means of optical microscopy of thin sections: loss of material through exfoliation lines or planes of macle which produces triangular and/or rectilinear holes; fissures through intergranular contact which in certain cases run throughout the crystals are shown. This microscopical morphology is probably due to the intergranular contact in the unaltered material (tangential to sutured-tangential) and the large thermal expansion anisotropy of the calcite crystals (temperature coefficients for the parallel and orthogonal directions in relation to the C axes in the field of room temperatures are 25.1×10^{-6} °C^{-1} and -4.9×10^{-6} °C^{-1}, respectively). Similar morphologies of weathering have been described [3, 12]. The fact that this process of microcracking does not occur on sedimentary limestones can probably be correlated to the structure of such a stone of sedimentary type and with very fine crystallization which by isotropic compensation does not feel the effect of interaction between crystals. The SEM has also permitted us to show a characteristic weathering morphology which is described in the following sections.

It is necessary to mention the great increase in porosity with the weathering (from 0.5% for the unaltered material to 5-6% for the very altered materials) that has been registered. Diverse porosimetric studies on altered samples indicate the apparition of meso- and macropores and the consequent loss of microporosity, which dominates the unaltered material. The average pore size distribution oscillates between 0.005-0.010 μm for the unaltered material, 0.050-0.150 μm for less altered marble and 5.400-7.500 μm for the very altered ones.

XRD studies do not reveal the presence of substances of which formation can be due to corrosion (chemical attack) phenomena; only small quantities of gypsum have been detected in some samples but their distribution and the existence of gypsum relieves in the upper zones which are periodically washed by the rain, indicate that only a simple deposition must be considered. The microscopical morphology of weathering due to the gypsum formation has been widely described [2-4, 6] and it is very different to those observed in the samples studied in this work. So, the EDS studies do not reveal the existence of sulphur compounds in the marble structure.

Artificially Altered Samples

All the samples submitted to the previously described thermohygrometric experiments and those from the monument show a very similar microscopical morphology. The most important weathering is produced in the material submitted to the complete cycle (-15°C to +80°C variations).

The study of the materials submitted to the subcycles reveals a more extensive weathering when the variations are from laboratory conditions to +80°C/95% RH, which seems to indicate that this process greatly contributes to the weathering processes; however, in the samples submitted to the other subcycle (-15°C to laboratory conditions) certain weathering manifestations also appear and a possible synergetic action should be considered.

The freeze/thaw cycles do not seem to modify the weathering micromorphology and the degree of alteration.

Weathering Stages

In Figure 1 the characteristic microscopical morphology of the unaltered material can be seen: large crystals and regular surface. Figure 2 shows the diverse stages established for the artificially altered material. In the first stage **(a)** the marble is covered on large zones by triangular pores of very diverse sizes. As the weathering advances **(b)**, a progressive increase in the pore size occurs with an incipient loosening of material; a typical morphology appears: a stepping surface with sharp edges. In a third stage **(c)**, the loss of material is more important and a rounding, fundamentally in the afore mentioned edges, occurs. In the last weathering process stage **(d)** a degradation of the surface occurs which leads to a disintegration of the material as well as the apparition of large and deep fissures. With the aim of adequately comparing the diverse microphotographs of the material from the monument with the acceleratedly alterated ones, similar magnifications have been used.

In Figure 3, we can observe that in the material from the Alhambra the 4 stages previously described also appear. The weathering morphology, specially that of the last stage of the process, explains the remarkable increase in porosity with the weathering as well as the new formation of meso- and macro-pores.

It is possible to conclude that the main weathering mechanism for the degradation observed in the white marble from the Alhambra of Granada is caused by the great climatic thermohygrometric variations.

Evaluation of the degree of weathering on the monument

The main visual indicators of weathering present in each of the patios and rooms studied are concisely described below; likewise, the equivalence of the more generalized microscopical morphology with the weathering stages previously established is indicated.

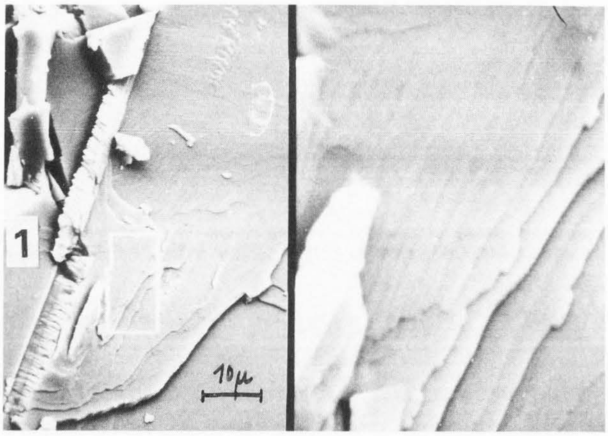
Patio de los leones. In this patio, totally outside, it is necessary to distinguish between the columns which surround the patio and the ornamental elements of the central fountain, the universally known lions.

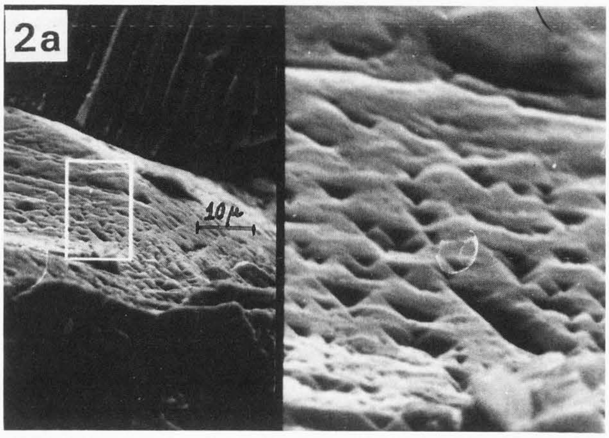
On the columns the main visual indicators of weathering are the fissures and cracks. However we must distinguish between a sunny zone, submitted to great thermic variations, in which the columns show an almost generalized important loss of material and disjunctions, and the non-sunny zone, in which the weathering manifestations are less important.

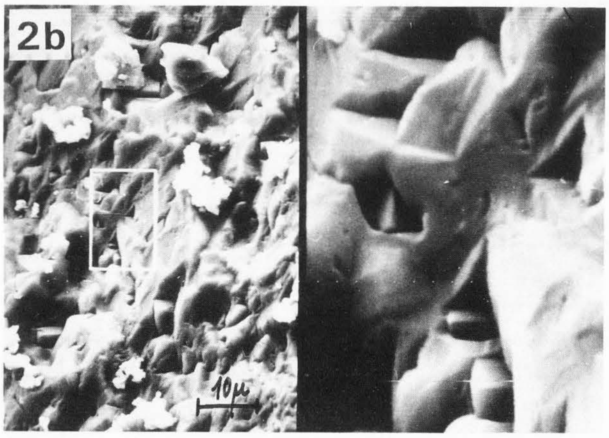
Figure 4 shows the more generalized microscopical morphology of the weathering for the materials from the sunny zone and we can consider, according to the stages established, that the materials are fundamentally in the third stage of the weathering process. Examples of all the stages can be found in all the columns.

The lions suffer, fundamentally, important losses of material; Figure 5 shows the more generalized microscopical morphology, which corresponds essentially to the last weathering process stage established. The high humidity to which these stony structures are submitted, their cyclic variations during the day due to the water being cut off and the poor state of conservation of the water pipes which are in the interior of the ornamental figures, concur with the simultaneous actions of other weathering mechanisms (principally freeze/thaw, salt crystallization, wetting/drying cycles and microbiological mechanisms [3]).

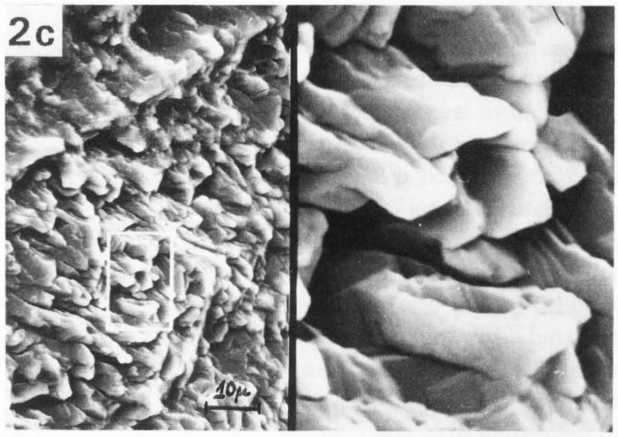
Annex rooms to the Patio de los leones. These are interior rooms and consequently the thermohygrometric variations are less important than outside; therefore, only some cracks and fissures are found as the more important visual indicators of weathering. The SEM study of a column sample reveals a general morphology (Figure 6) which corresponds to the initial stage of weathering. The apparition of small triangular holes on the matrix can be observed.







Arrayanes Palace. In this zone of the monument the loss of material is common, and specially in the "Patio de Comares"; likewise, the cracks and fissures are frequent. Figure 7 (which corresponds to an ancient remain of pavement) shows a material in advanced state of weathering (3rd-4th stage of the established process).



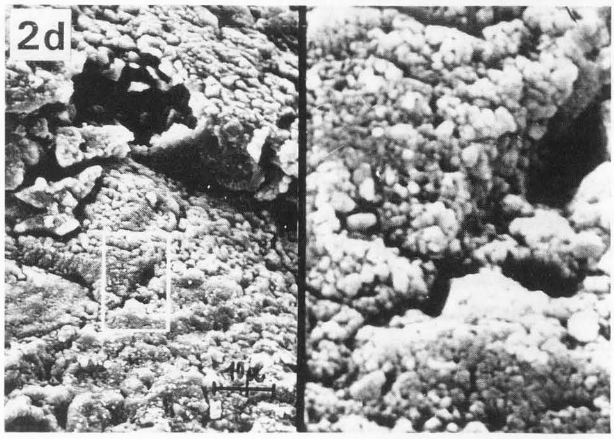


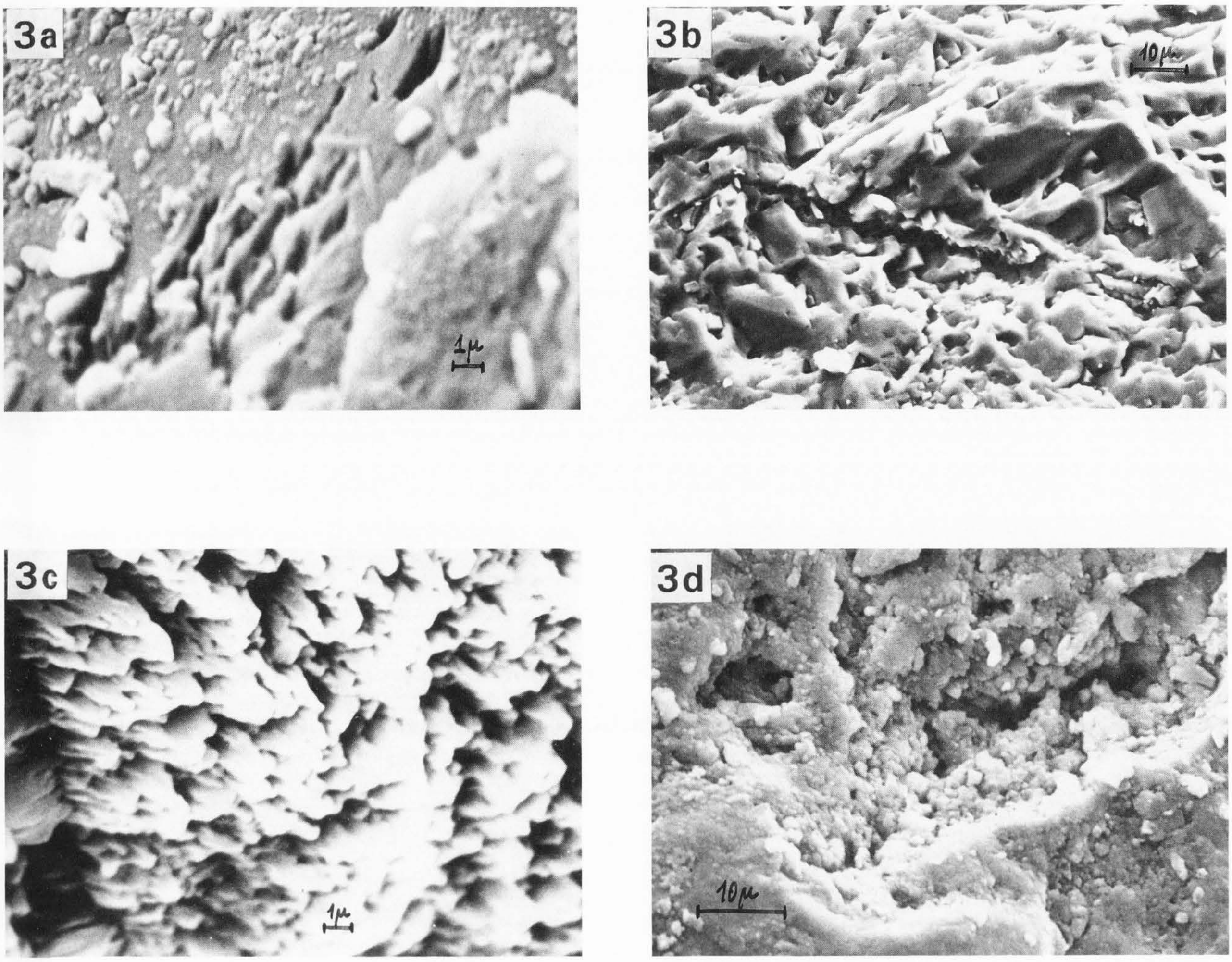
Figure 1. SEM micrograph of the unaltered white marble from Macael quarries. Bar = 10 μm. Right: ten times enlargement of boxed area in left figure.

Figure 2. Artificially established stages of the weathering process. Bar = 10 μm. Right: ten times enlargement of boxed area in left figure.

Lindaraja. On the columns of this zone, macroscopical indicators of weathering such as cracks, fissures and loss of material have been observed but less important than the Arrayanes Palace. The photomicrographs of Figure 8 show a material which can be considered between the second and third weathering stages.

Conclusions

The predominant morphology of weathering in the white marble used in the Alhambra of Granada is essentially due to the great thermohygrometric variations



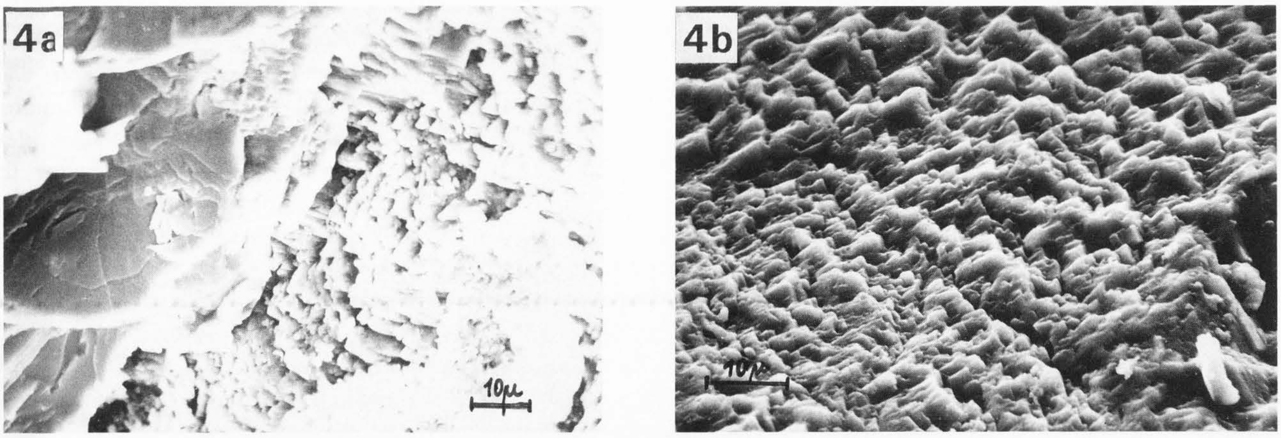
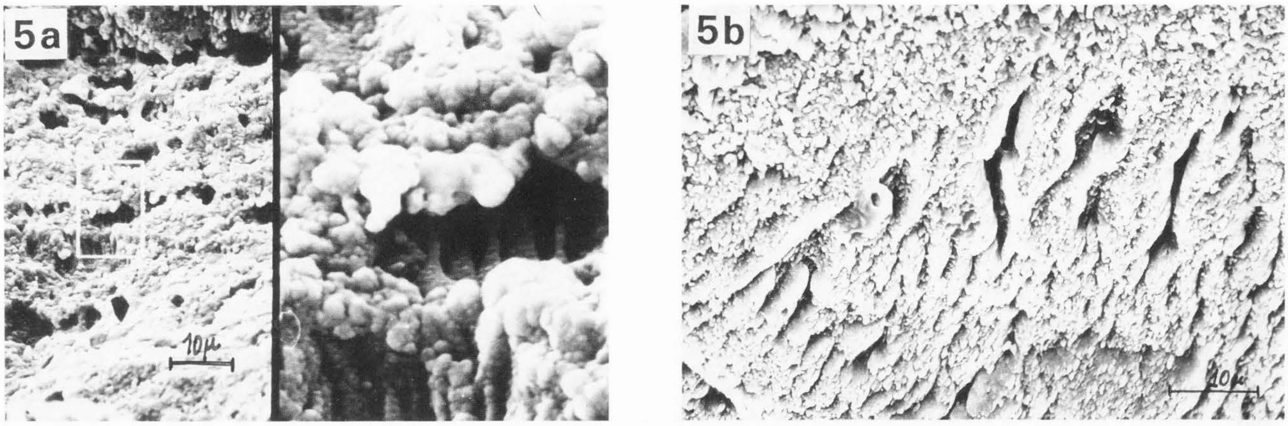


Figure 3. Weathering stages on the white marble from the Alhambra. Bars = (a, c) 1 μm; (b) 10 μm; (d) 10 μm).

Figure 4. Altered marble from the columns of the Patio de los leones Bars = (a, b) 10 μm.



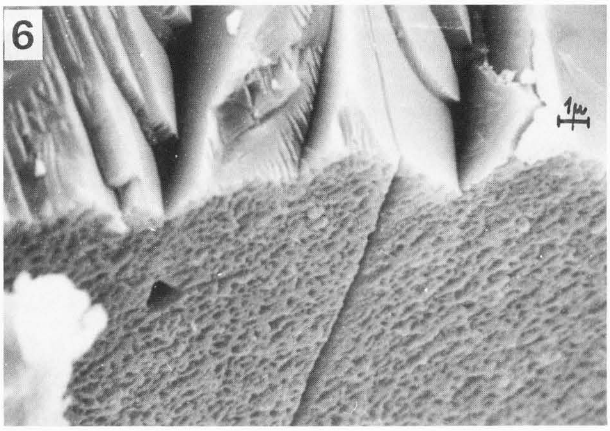


Figure 5. Altered marble from the lions of the Patio de los leones. (a) Bar = 10 μm; right: ten times enlargement of boxed area in left figure; (b) Bar = 10 μm.

Figure 6. Altered marble from a column of the annex rooms to the Patio de los leones. Bar = 1 μm.

Figure 7. Altered marble from an ancient remain of pavement of the Arrayanes Palace. Bar = (a) 10 μm; (b) 1 μm.

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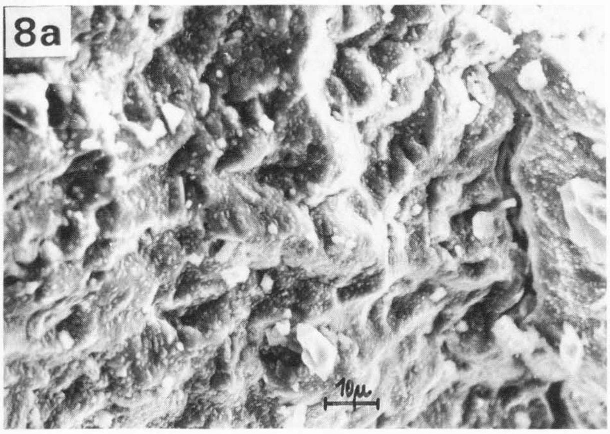
which can or cannot include freeze/thaw cycles. The effect on the marble weathering of these factors are well described [3, 4, 10, 12] and considered by many authors as the main factor of the physical decay of the marbles; the weathering micromorphology is function of the marble structure and composition, however, certain similitudes can be observed; the intergranular decohesion is the main and common result.

The accelerated weathering experiments and the studies by SEM have permitted us to establish four successive stages in the weathering process which permits the objective evaluation of the degree of weathering of some materials from the monument.

The importance of the electron microscopy in the study of the weathering processes in certain stones has been demonstrated, specially for those materials in which the accelerated weathering experiments do not provoke appreciable macroscopical alterations in a reasonable period of time.



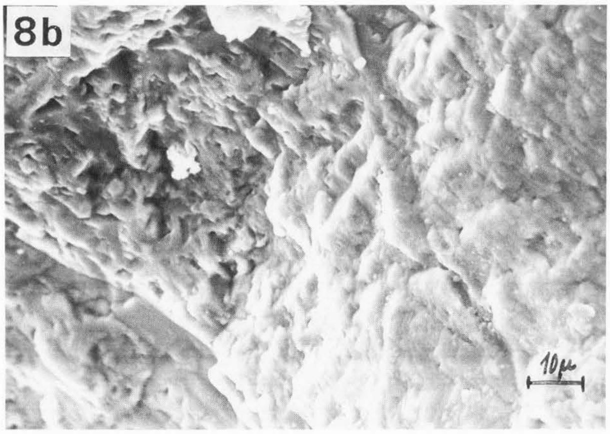


Figure 8. Altered marble from the columns of Lindaraja. Bar = 10 μm.

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Discussion with Reviewers

Reviewer I: The qualitative examinations of surface topography are sufficient to propose weathering mechanisms?

Authors: If the EDS and XRD studies do not reveal the presence of substances of which formation can be due to corrosion phenomena (chemical weathering), the qualitative examination of the surface topography is sufficient to propose weathering mechanisms, in this case due to thermohygrometric variations; other weathering factors have been studied and the corresponding micromorphologies compared with those of the monument materials with negative results. So, the development of the weathering in the monument materials has been reproduced by laboratory accelerated weathering experiments which confirmed the proposed mechanism.

R.N. Butlin: Why is SEM an adequate method for the study of the weathering mechanisms of very compact stone materials?
Authors: SEM is adequate since it allows observations of microscopical weathering of the materials submitted to the accelerated weathering experiments and their comparison with the monument materials in a reasonable period of time. Macroscopical changes need a large number of weathering cycles, and the visual observations do not permit to establish the weathering development and their comparison with the monument materials for the establishment of the weathering mechanism.

R.N. Butlin: Why were the conditions in the tests -15 $\pm$ 0.5°C to +80 $\pm$ 0.5°C and 95% RH for 10 hours then 14 hours at laboratory temperature?
Authors: The accelerated weathering experiments try to consider the environmental conditions but the cycles must be more aggressive for the acceleration of the weathering processes. Therefore, the high number of days/year with temperatures lower than 0°C are considered by the freeze/thaw cycles, temperatures between -10 and -20°C are frequently described in the bibliography (i.e. NBN B05-203). High thermohygrometric variations also occur in the monument, and temperatures of approximately 50°C can be measured on the stones, for this reason, 80°C and 95% HR have been used in the accelerated weathering experiments.

R.N. Butlin: Why 80 cycles?
Authors: The number of cycles is 80 because at this number, the 4th microscopical weathering stage was reproduced. For the macroscopical weathering, a very high number of cycles is necessary; nowadays, some samples having submitted to the thermohygrometric cycles with a number of cycles >300 and macroscopical weathering has still not been observed.

R.N. Butlin: Why were freeze/thaw cycles used?
Authors: Freeze/thaw cycles have been used due to the environmental conditions (high number of days/year with temperatures lower than 0°C), and they must be important in those ornamental materials of the fountains which are submitted to high humidity and when the temperature decreases, freeze/thaw processes must to occur.